

## REMARKS

### The Amendment

Applicants have amended claims 47, 50, 52 and 55 and added new independent claims 56-58.

The amendments to claims 47, 52 and 55 should obviate the indefiniteness rejections under 35 U.S.C. 112. The indefiniteness of "elevated temperature" in claim 47 is obviated as the amended claim no longer recites this phrase. Claim 52 has been amended to recite polyethylene powder and thus has antecedent basis in the independent claim. The objectionable "first mixture" recitation has been deleted. Claim 55 has been amended to recite the density units as grams/cubic centimeter. Enclosed with this response is a copy of a publication which evidences that those skilled in the art use grams/cubic centimeter as the unit of density when referring to polymers, specifically when referring to polyethylene. The enclosed publication, *Polymer Handbook*, has a copyright date of 1989 and evidences that the unit of density of polyethylene used in the art was grams/cubic centimeter ( $\text{g cm}^{-3}$ ). References to that unit of measurement are highlighted at numerous locations in the text and in particular, note the reference to the ASTM D792 standard for density on page V/23 of the publication.. Accordingly, this amendment does not constitute new matter. A similar amendment has been made to the specification on page 4, line 20.

Applicants have submitted three independent claims which are substantial duplicates of claim 47 with the single exception that each recites alternative wording for the phrase "to incorporate" which appears at line 17 of claim 47. Newly added claim 56 recites: "to blend", newly added claim 57 recites "to mix"; and newly added claim 58 recites "to fuse". The reasons for submitting substantially duplicate claims will be apparent in the discussion of in the following section entitled: Responses to the 103(a) Rejections.

Response to the "enabling" Rejection

Oddly, the claims have been rejected under the provisions of the first paragraph of 35 U.S.C. 112 for an alleged lack of teaching in the specification. The first paragraph of 35 U.S.C. 112 addresses the requirement of the specification that it contain a written description of the invention and the manner and process of using it ...to enable any person skilled in the art.. to make and use it. The examiner, however, admits that the specification teaches those skilled in the art how to make and use the invention, and that the specification is enabling for the composition recited by original claim 1. Contrary to the examiner's assertion, there is no provision in first paragraph of 35 U.S.C. 112 that requires the specification to be commensurate in scope with the claims, as that would result in claims always limited to the best mode of practice.

The examiner also stated that there "is no evidence that limitations outside the scope of the originally filed claim 1 would be operative. This is a non-statutory rejection, and is clearly improper, as it is not the function of claims to exclude all possible inoperable conditions. Applicants acknowledge that a claim which has an inoperable or impossible limitation may lack an enabling disclosure, *Raytheon Co. v. Roper Corp*, 724 F.2d 951, 956, 220 USPQ 592, 596 (Fed Cir 1983). However, such is not the case with the instant claims which do not recite inoperable limitations. Instead, claims are improper only if "the number of inoperative combinations becomes significant, and in effect forces one of ordinary skill in the art to experiment unduly in order to practice the claimed invention"; *Atlas Powder Co. v. E.I.Du Pont De Nemours & Co*, 750 F.2d 1569, 1576-77, 224 USPQ 409, 414 (Fed. Cir. 1984). One skilled in the art does not need to experiment unduly, in fact, does not need to experiment at all, for the specification clearly teaches the practice of the invention. Reconsideration of this rejection is respectively requested.

Responses to the 103(a) Rejections

A. The Howell et al Rejection

Claims 47-53 and 55 were rejected under 35 USC §103 as considered by the examiner to be obvious from the teachings of Howell et al.

Howell et al disclose a polyethylene coating which is applied to paper to impart water resistance. The polyethylene powder is suspended in a liquid carrier which can be water or an organic solvent. When water is used as the carrier, a latex additive can be included in the coating dispersion. The paper is coated with the dispersion and placed in a hot air oven to fuse the polyethylene.

The latex additive is disclosed as only useful with water; see column 3, lines 72-73 ("adding a minor amount of a latex to the water dispersion.") and the exclusion of the latex when using mineral spirits; see Example IX. Further, none skilled in the art would attempt to prepare a coating composition by mixing a latex (water dispersion) with an organic solvent as the two components are immiscible.

Further, the latex additive is a rubber latex; see claim 1 "a rubber latex" and claims 7 and 8 which define the "rubber latex" as either styrene-butadiene or polyvinylidene chloride.

If the patentees had confined their disclosure to the scope of their invention, i.e., the coating of paper substrates, it is doubtful that the examiner would have ever considered basing a rejection on this patent. Nevertheless it is noted that Howell et al disclose the coating of a "substrate" which can include "other plastics"; column 2, line 70. The only plastics specifically identified in Howell et al are polyolefins and polyethylene which are used in the coating dispersion. Howell et al state:

As discussed above, various substrates may be coated with the polyolefinic polymers in accordance with the present invention. Such substrates include, for example, paper, cloth glass, wood, other plastics, metal, ... (underlining added)..

Thus one is forced to conclude that Howell et al suggest the application of the

polyolefin (polyethylene) dispersion to plastics other than polyolefins or polyethylene.

The claims have been amended to recite that the liquid carrier is an inert organic solvent, examples of which can be found on page 5, lines 35-37 and on page 8, lines 15-18 of the parent application, Ser. No. 08/566,906. With this amendment, the only relevancy of Howell et al is a disclosure that polyethylene powder can be dispersed in an organic solvent and used to coat a substrate (other than a polyolefin) and which is heated to fuse the coating. There is no suggestion to use an adhesive resin in the organic-solvent coating composition since, as pointed out above, Howell et al only suggest use of the rubber latices with water.

The claims even prior to this amendment distinguished over Howell et al in that the claims recited the application of a coating containing polyethylene particles applied to an object of polyethylene, thus not to a substrate of an "other" plastic as suggested by Howell et al. From the preceding remarks it must be clear without question that Howell et al is not relevant prior art to the claims as amended herein.

#### B. The WO 96/23041 Rejection

Claims 47-53 and 55 were also rejected under 35 USC §103 as considered by the examiner to be obvious from the teachings of Applicants' prior PCT publication, WO 96/23041.

The prior WO 96/23041 publication does not defeat patentability of the claims of this application for a number of reasons. First, the publication is not a reference as the claims of this application are supported in applicants' parent application which was filed prior to the publication date of WO 96/23041. Further, even if the examiner does not credit the claims with the priority date of the parent application, the WO 96/23041 publication does not teach those skilled in the art the specific method claimed which comprises application of a coating composition containing polyethylene powder to a polyethylene surface.

#### Applicants' Priority Claim

Applicants contend that WO 96/23041 is not applicable as a prior art reference, as the claims of this application are supported in applicants' prior application, Serial No. 08/566,906, which was filed prior to the August 1, 1996 publication of WO 96/23041. In the preliminary amendment, Applicants referred to U.S. Patent 5,745,961 which is the patent that issued on the 08/566,906 application. As noted from the Office action, Applicants should have referred to the application, rather than the issued patent. In any event, claim 47 is supported in the parent application for reasons previously argued.

Newly added claims 56-58 differ from claim 47 in only a minor regard. Claim 47 recites heating the decorative coating composition and polyethylene surface to "incorporate" the decorative coating composition into the polyethylene surface. As previously argued, that is supported by the following disclosure in the parent application:

It is believed that the enhancement solid forms an outer surface or skin on the molded product substantially entirely of the enhancement solid and that the enhancement solid also mixes with the molding resin during the molding step, so that at increasing depth into the wall of the molding product, the enhancement solid decreases, and the molding resin increases, in concentration. (page 12, lines 3-9 Ser. No.08/566,906)

Newly added claim 56 recites "to mix" rather than "to incorporate", thus using the identical expression in the parent application. Claim 57 recites "to fuse" rather than "to incorporate". Claim 58 recites "to blend" rather than "to incorporate". All of these expressions are substantially identical in meaning and context. *Webster's Seventh Collegiate Dictionary* defines "fuse" as "to blend by melting together"; identifies "mix" as a synonym; and defines "mix" as "to combine or blend into one mass".

The fact that the precise words in claim 47 are not present in the parent

application does not preclude a finding that the claims are supported in the parent application. As stated by the Federal Circuit in *Ralston Purina Co. v. Far-Mar-Co., Inc.* at 227 USPQ 177, 181-82 (Fed. Cir. 1985):

The invention claimed in the later application does not have to be described in the prior application *in ipsius verbis* in order to satisfy the description requirement of section 112. Martin v. Johnson 454 F 2d 746, 751, 172 USPQ 391, 395 (CCPA 1972); see *Case v. CPC International, Inc.*, 730 F.2d 745, 751, 221 USPQ 196, 201 (Fed. Cir.) ..... Thus, the test for determining whether the disclosure complies with the written description of the invention requirement is whether it would have reasonably conveyed to one of ordinary skill that the inventor invented the later-claimed subject matter. *In re Kaslow*, 707 F.2d 1366, 1375, 217 USPQ 1089, 1096 (Fed. Cir. 1983).

Applicants do not intend to seek a patent with identical claims and will cancel the substantial duplicates once any of claims 47 and 56-58 is considered to be patentable. It is the opinion of Applicants' attorney that all are supported in this and the parent application, and are patentable. The alternative wording is submitted so as not to preclude applicants from obtaining protection by being denied on semantics.

Applicants have chosen to submit a generic claim to the methods of the applications in this continuation application. Subject only to a possible requirement for a terminal disclaimer, applicants are clearly entitled to submit the generic claim in this manner. As the generic claim (47) is entitled to patentability, the dependent claims are similarly patentable.

#### The inadequacy of the teaching in WO 96/23041

The WO 96/23041 publication contains the following disclosure of the polyolefin powder which is used in the coating composition:

The particulate polyolefin means that are used in the thermoplastic spray material should be a polyolefin powder. In its preferred

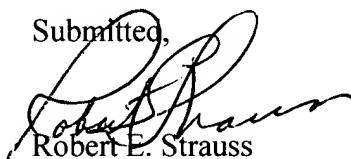
embodiment, the polyolefin powder would have a particle size of less than 50 microns. Although a polyolefin powder having a particle size greater than 50 microns may be used, these types of powders have a tendency to clog a nozzle 11a of a canister 11. (Paragraph bridging pages 18 and 19. Essentially the same disclosure is found at multiple locations throughout the specification.)

Polyethylene is not identified as a useful polyolefin powder, and no example of a specific spray composition is given in the specification. Applicants' claims are limited to combining a decorative enhancement composition containing polyethylene powder with a polyethylene surface. This specific combination is not disclosed in the WO 96/23041 publication.

Applicants have found that polyethylene powder when combined with a polyethylene surface of a polyethylene article in the presently claimed method achieves results far superior to the use of any other polyolefin, and specifically superior to the use of the next adjacent homologue, i.e., polypropylene, as the polyolefin powder. These results are not suggested or taught by the WO 96/23041 publication.

In summary, applicants submit that the WO 96/23041 publication is not applicable as a prior art reference as the present claims are supported in applicants' patent application. Even, however, if the examiner does not consider the publication to be removed as a reference, the instantly claimed subject matter is not obvious from the WO 96/23041 publication.

The claims are of proper form and recite patentable subject matter over the prior art. Examination and allowance are respectfully requested.

Submitted,  
  
Robert E. Strauss  
Reg. No. 19,364

## APPENDIX

47. (**Amended Herein-Fourth Amendment**) A method for decorative enhancement of a polyethylene surface of a molded polyethylene article, which method comprises the steps of:

- (a) combining a decorative enhancement composition and said polyethylene surface wherein said decorative enhancement composition consists essentially of:
  - (1) an inert organic solvent [a liquid carrier] that provides the decorative enhancement composition with a consistency and viscosity for liquid methods of application;
  - (2) a colorant to impart a surface color;
  - (3) a binder selected from the class consisting of aromatic and aliphatic hydrocarbon resins, waxes, rosins, and terpene-based resins; and
  - (4) polyethylene powder; and
- (b) heating said decorative enhancement composition and said polyethylene surface [to an elevated temperature and time sufficient] to incorporate said decorative enhancement composition into said surface and produce a molded polyethylene article having said surface

decoratively enhanced by said colorant.

50. (**Amended**) The method of Claim 49 wherein said heating step is accomplished by heating said decorative enhancement composition and said surface of said preformed rotationally molded polyethylene article [to a temperature and for a time sufficient] to fuse said decorative enhancement composition into said surface. [to said preformed rotationally molded polyethylene article.]

52. (**Twice Amended**) The method of Claim 47 wherein said colorant, said binder and said particulate thermoplastic powder collectively comprise [a first mixture comprising] 10 to 80 weight percent of said decorative enhancement composition.

53. (**Amended**) The method of claim 52 wherein said colorant comprises 9 to 50 weight percent of colorant, binder solid and polyethylene, [said first mixture and said binder] and said polyethylene powder collectively comprises 50 to 91 weight percent of colorant, binder solid and polyethylene. [said first mixture.]

55. (**Twice Amended**) The method of Claim 53 wherein said polyethylene powder has a density from 0.88 to 0.97 grams/cubic centimeter and a particle size no greater than 140 microns.



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# POLYMER HANDBOOK

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Edited by

**J. BRANDRUP and E. H. IMMERMUT**



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# Physical Constants of Poly(ethylene)\*

R. P. Quirk and M. A. A. Alsamarraie  
 Institute of Polymer Science, University of Akron, Akron, Ohio

TABLE I: GENERAL PROPERTIES

**Bond Angle and Bond Length**

	X-Ray (1-3)(°)	Neutron Scattering (4)	Temp
BOND ANGLE (IN DEGREES)			
C-C-C	112.0	107.7	(4 K)
		108.1	(90 K)
H-C-H	107.0	109.0	(4 K)
		110.0	(90 K)
BOND LENGTH (Å)			
C-C	1.53	1.578	(4 K)
		1.574	(90 K)
C-H	1.069	1.06	(4 K)
		1.07	(90 K)

\*Measurements taken at room temperature.

**Chain Branching (short)  
 Effect on Density and Refractive Index. (5,6)**

Methyl Groups per 1000 C Atoms	Density [Mg m <sup>-3</sup> = g cm <sup>-3</sup> ]	Refractive Index $n_D^{25}$
83	0.91	1.5060
48	0.917	1.5168
46	0.925	1.5152
26	0.929	1.5227
16	0.926	1.5260

**Effect on Expansion Coefficient (mean) and Specific Volume  
 of Crystalline Phase. (6,7)**

Methyl Groups per 1000 C Atoms	(1/V <sub>20</sub> ) -150 to 100°C	(ΔV/ΔT) × 10 <sup>4</sup> 0 to 100°C	V <sub>20</sub>
0.3	2.47	3.13	1.001
2	2.59	2.95	0.998
17.5	2.61	2.98	1.010
23	2.84	3.42	1.009
37	2.96	3.70	1.017

**Effect on Long Period Spacings and Crystallinity of Completely Annealed Samples. (6,8)**

Poly(ethylene)	Methyl Groups per 1000 C atoms	Long Period Spacing [Å]	% Crystallinity	Ref.
Branched (high pressure)	60	220	21	9
	45	200	48	
	35	210	50	
	28	220	53	
	20	230	56	
	15	250	59	
	10	260	62	
Linear (Ziegler Type Catalysts)	7	320	77	5,7
	5	360	79	
Linear (Phillips Petroleum Process)	2	420	88	10

\*Based on a table in the second edition by S. L. Aggarwal, The General Tire and Rubber Company Akron, Ohio.

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**Chain branching (cont'd)**

**Effect on Melting Point.** (Both the amount and randomness of branching affect the melting point. Experimental conditions used for the following data were not adequate for equilibrium crystallinity and accuracy of melting points). (6)

Methyl Groups per 1000 C atoms	Melting Point [°C]
87	105
28	113
28	108
8	123
0	132 (?)

**Coefficient of Thermal Expansion.  
Branch d polyethylene. (6,11)**

Temp [°C]	Coefficient of Expansion × 10 <sup>3</sup>		Specific Volume <sup>a</sup> Ratio ( $V_E/V_{25C}$ )
	Linear	Cubical	
-35	10.0	30	0.969
20	13.7	41	0.975
0	18.3	55	0.986
20	23.7	71	0.997
25	24.8	74	1.000
40	29.0	87	1.012
60	33.7	101	1.031
80	40.3	121	1.055
100	46.6	140	1.094
110	51.0	153	1.130
115	25.0	75	1.140
115-150	25.0	75	—
150	25.0	75	1.168

<sup>a</sup> $V_E$  is relative excess volume,  $V_{25}$  is the volume at 25°C.

Data for amorphous linear poly(ethylene); see Ref. 12.

**Crystallinity\***. Depends upon chain branching; the following are some representative values of typical commercial poly(ethylenes) (13).

	Average Molecular Weight	Density $\rho$ (g/cm <sup>3</sup> )	Melting Point T°C	Degree of Branching (CH <sub>3</sub> /100C)	Crysta- llinity ( $\alpha_c$ )	Crysts thickne s (Å)
Marlex 6015	$15.0 \times 10^4$	0.980	131	0.05	0.94	239
Hostalen GC	5.0	0.969	129	0.10	0.83	198
Hostalen GF	12.0	0.968	128	0.64	0.85	184
Hoechst PA-190	0.9	0.954	124	0.84	0.76	141
Alkathene HD	24.5	0.952	121	0.91	0.76	120
Epolene C-11	1.0	0.947	119	1.08	0.74	110
Lupolen KR 1051	5.1	0.943	120	1.30	0.70	114
BASF a Wachs	1.0	0.933	111	1.84	0.67	81
Lupolen KR 1032	5.3	0.931	115	2.50	0.60	92
Epolene C-13	1.0	0.919	104	2.80	0.54	65
Lupolen 1810 H	5.4	0.928	106	3.00	0.59	65
Hoechst PA-130	$3.0 \times 10^3$	0.957	115	1.58	0.85	9
Epolene N-10	2.5	0.925	105	2.25	0.61	6
Epolene N-12	1.5	0.941	108	2.27	0.75	6
BASF a Wachs	5.6	0.936	106	2.32	0.68	6
Epolene N-11	1.5	0.934	104	2.48	0.68	6
Hoechst PA-560	6.0	0.914	101	4.10	0.51	5
Epolene C-10	7.0	0.919	99	4.19	0.60	6
Epolene C-101	3.2	0.936	104	4.42	0.70	6
Hoechst PA-520	2.0	0.917	102	4.90	0.54	5
Epolene C-12	3.7	0.906	83	6.94	0.50	—

\*Crystallization from melt by rapid cooling at ambient temperature. Crystallinity estimated from density.

**Crystallization Kinetic Parameters.** See table "Rate of Crystallization of Polymers" in this Handbook and Refs. 14,15.

**Crystallographic Data and Crystallographic Modifications.** (16,17)

Crystal System	Space Group	Lattice Constants (Å)			$\alpha$ , $\beta$ , or $\gamma$ (deg.)	Number of Chains per Unit Cell	Molecular Conformation	Crystal Density (g cm <sup>-3</sup> )
		<i>a</i>	<i>b</i>	<i>c</i>				
Orthorhombic stable form	Pnam-D <sub>2h</sub>	7.417	4.945	2.547		2	Planar	1.31
Monoclinic metastable form	C2/m-C <sub>2h</sub>	8.09	f.a. <sup>a</sup> = 2.53	4.79	$\beta = 107.9$	2	Zigzag (2/1) Planar	1.00
Orthohexagonal (assumed) High-Pressure form		8.42	4.56		f.a. <sup>b</sup>		Zigzag (2/1)	0.998

<sup>a</sup>f.a. indicates fiber axis.

<sup>b</sup>f.a. has not been determined.

## Crystallographic Data cont'd

## Temperature Dependence of Crystallographic Data for Orthorhombic Poly(ethylene). (16)

Temperature (K) <sup>a</sup>	Lattice Constants (Å)			Specific Volume (cm <sup>3</sup> /g)	Refs
	<i>a</i>	<i>b</i>	<i>c</i>		
4 <sup>b</sup>	7.121	4.851	2.548	0.945	4
10	7.16	4.86	2.534	0.947	25
77	7.18	4.88	2.534	0.953	25
77	7.155	4.899	2.5473	0.959	26
90 <sup>b</sup>	7.161	4.866	2.546	0.953	4
195	7.27	4.91	2.534	0.971	25
293 <sup>c</sup>	7.399 (7.432)	4.946 (4.945)	2.543 (2.543)	0.999 (1.003)	18
297	7.42	4.96	2.534	1.001	25
297	7.40	4.93	2.534	0.993	1
297	7.36	4.92	2.534	0.985	27
303	7.414	4.942	2.5473	1.002	26

<sup>a</sup> Data obtained by X-ray diffraction studies unless otherwise indicated.<sup>b</sup> Data obtained by neutron diffraction.<sup>c</sup> The data of nonoriented samples are given without parentheses and those of oriented samples are given with parentheses, both for high-density PE.

**Density.** [Mg m<sup>-3</sup>] ≡ [g cm<sup>-3</sup>] (see also Table II and III.) Unless otherwise stated, the values of density are given for 25°C.

	Value	Refs.
Amorphous (from extrapolation of data above the melting point)	0.855	20
Commercial high-pressure poly(ethylene)	0.915 – 0.935	29
Experimental high-pressure poly(ethylene)	0.940 – 0.970	29
Ziegler process (Ref. 30,31) poly(ethylene)	0.940 – 0.965	29
Phillips process (Ref. 10) poly(ethylene)	0.960 – 0.970	29
Crystal density (theoretical)	see Crystallographic Data and Crystallographic Modifications	

## Dimensions of Linear Polyethylene Molecules. Effect of Temperature and State, Neutron Scattering Measurements.

Temperature (°C)	PEH Matrix	PED <sup>a</sup>			
		$\bar{M}_w \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\langle S^2 \rangle_z^{1/2} b$ (Å)	$\langle S^2 \rangle_w^{1/2} c$ (Å)
23	78	60	133	0.46	Crystalline
150	100	140	215	0.46	Molten
150	80	10	43.8	0.44	Molten

<sup>a</sup> PED is deuterated polyethylene.<sup>b</sup>  $\langle S^2 \rangle_z^{1/2}$  is the z-average of the radius of gyration of the molecule.<sup>c</sup>  $\langle S^2 \rangle_w^{1/2}$  is the weight-average value of the radius of gyration of the molecule.

**Molecular Dimensions of Linear Poly(ethylene) (Unperturbed)** In tetralin at 105°C.  $\langle r_o^2 \rangle_w$  is the weight-average mean-square end-to-end distance in nm;  $M_w$  is the weight average molecular weight;  $D$  is the diameter of a spherical segment of the lattice model chain; and  $r_{max}$  is the length of the fully extended chain. (35).

$M_w \times 10^{-5}$	$((r_o^2)_w/M_w)^{1/2}$ [nm/(g/mole) <sup>1/2</sup> ]	$((r_o^2)_w/Dr_{max})$
1.25	0.192	0.780
2.69	0.215	0.986
4.65	0.190	0.773

Temperature dependence of  $\langle r_o^2 \rangle$  (in long chain paraffinic hydrocarbon solvents),  $-d \ln \langle r_o^2 \rangle / dT = 1.2 \times 10^{-3}$ . (36).

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**Elastic Compliance.** See Table II.

**Electrical Properties.** (See also Table III.) (37).

**Dielectric Constant.** at 100 kc at 23°C: 2.3. (38).

**Effect of Density.\*** (39).

Density (g/cm³)	Dielectric Constant (ASTM D-150)
0.920	2.28
0.925	2.29
0.930	2.30
0.935	2.31
0.940	2.32

\*The relationship shown in this table is for pure poly(ethylene). Therefore, considerable divergence from this relationship is caused by the presence of impurities as well as addition of additives such as carbon black or other fillers.

**Dielectric Loss.**  $\tan \delta 1 \times 10^{-4} - 1 \times 10^{-3}$ . (40,41).

The values of  $\tan \delta$  depend on temperature and structure of poly(ethylene). (40).

**Effect of Molecular Weight on Paraclustering.** For deuterated poly(ethylene) in a protonated poly(ethylene) matrix with molecular weight ca. 100,000 by neutron scattering measurements.<sup>a</sup> (34).

Molecular Weight of Tagged Molecules	$\frac{\Sigma_0}{M_w} = \frac{\text{Molecular Weight (neutrons)}}{\text{Molecular Weight (g.p.c.)}}$	$\frac{\langle S^2 \rangle_v^{1/2}}{\bar{M}_w^{1/2}}$
3000	$73 \pm 7$	4.1
12000	$7 \pm 1$	1.8
60000	$0.91 \pm 0.1$	0.49
140000	$0.94 \pm 0.1$	0.42

<sup>a</sup> All samples solution blended in ortho-dichlorobenzene, quenched rapidly from the melt and measured at 25°C (concentration of tagged molecules  $\leq 5\%$ ).

<sup>b</sup>  $\langle S^2 \rangle_v^{1/2}$  the weight-average value of the radius of gyration of the molecule in  $\text{\AA}/(\text{g/mol})^{1/2}$

**Dielectric Strength.** (42).

Temperature (°C)	Value $\times 10^{-6}$ (V cm <sup>-1</sup> ) <sup>c</sup> , <sup>d</sup>
-200 to 0	7
50	5.3
100	1.8

<sup>c</sup> Short-time test value (ASTM D149) is 16000–24000 V cm<sup>-1</sup>, and depends upon sample configuration and impurities. (43).

<sup>d</sup> Intrinsic dielectric strength of LDPE is on the order of  $8.0 \times 10^5$  V cm<sup>-1</sup> if all chain end, surface and impurity effects are eliminated. (43).

**Elongation at Break.** [%] See Table III.

**Enthalpy, Entropy.** See Thermodynamic Properties.

**Entropy of Fusion.** [J mol<sup>-1</sup>K<sup>-1</sup>]

	Value	Ref.
$\Delta S_f$	9.81	44
	9.60	45
	9.91	46
At constant volume ( $\Delta S_v$ )	7.42	45
	7.72	47

**Flash Ignition Temperature.** ASTM Method E136-58T: 340°C. (48).

**Frictional Properties.** (49).

Coefficient of Friction ( $\mu$ )	Steel Sliding on Polymer		Polymer Sliding on Steel		Polymer Sliding on Polymer	
	Polished	Abraded	Polished	Abraded	Polished	Abraded
Static ( $M_s$ )	0.60	0.33	0.60	0.33	0.60	0.33
Kinetic ( $M_k$ )	0.60	0.33	0.60	0.33	0.60	0.33
	0.50	0.25				

**Glass Transition Temperature (°C)<sup>a</sup>.** (50).  
See also Transition Temperatures

Value	Refs.
-30 ± 15	51,52
-80 ± 10	53
-128 ± 5	12,54

<sup>a</sup>Considerable disagreement exists between different authors on the exact value of the transition which can be identified as the glass transition temperature. See Ref. 50 for detailed discussion.

**Glass Transition Activation Energy.** 46–75 kJ mole<sup>-1</sup>. (55).

**Hardness, Shore D.** See Table III.

**Heat Capacity, Specific.** See Thermodynamic Properties.

#### Heat of Combustion

Density [Mg m <sup>-3</sup> ] ≈ [g cm <sup>-3</sup> ]	Methyl Groups per 1000 C Atoms	Heat of Combustion ΔE [kJ kg <sup>-1</sup> ]
0.9391	8.3	-46,412
0.9220	24.7	-46,492
0.9053	46.2	-46,542

#### Heat of Fusion

T (K)	ΔH (kJ mole <sup>-1</sup> )	T (K)	ΔH (kJ mole <sup>-1</sup> )	Ref.
260	3.050	370	4.000	
270	3.149	380	4.051	
280	3.244	390	4.084	
290	3.338	400	4.101	
300	3.430	410	4.105	
310	3.520	414.6	4.100 ± 0.2	57
320	3.609	420	4.090	
330	3.696	430	4.060	
340	3.781	440	4.011	
350	3.881	450	3.944	
360	3.936	460	3.859	

**Melting Temperature.** [°C]<sup>a, b</sup>

	Value	Ref.
Poly(methylene)	136.5 ± 0.5	80
Linear Poly(ethylene)	137.5	45
Linear Poly(ethylene), High Molecular Weight Fraction	138.5	81
From Extrapolation of M.P. of <i>n</i> -Paraffins	141 ± 2.4	82
T <sub>m</sub> (∞ MW)	141.4–145.5 ± 1 <sup>b</sup>	14

<sup>a</sup> See also Table II and Chain Branching, effect on melting temperature.

<sup>b</sup> The estimated melting point of the infinite poly(ethylene) crystal is in dispute (see Ref. 14).

**Melt Viscosity.** See Table II.

**Heat of Fusion (cont'd)**  
From differential thermal analysis data

Poly(ethylene) Type	Melting Point [°C]	Heat of Fusion [kJ kg <sup>-1</sup> ]	Ref.
Marlex 50 (Phillips, Linear)	135	245.3	58
Super-Dylan (Ziegler, Linear)	130	218.6	58
DYNH (Union Carbide, branched)	112	140.6	58
Linear Poly(ethylene)			
from dilatometric measurements:		280.5	45
from calorimetric measurements		277.1	46,59

**Ignition Limiting Oxygen Indices.** (ILOI)<sup>a</sup>. (60).

650°C	600°C	550°C
2.8 ± 0.1	3.5 ± 0.1	5.7 ± 0.1

<sup>a</sup>This method (ASTM D2863-70) is defined as the minimum volume fraction of oxygen required for ignition to occur.

**Impact Strength, Izod.** See Table III.

**Infrared Absorption Bands.** (61–68).

**Far Infrared.** (69).

**Intrinsic Viscosity.** See Table II.

**Low Temperature Brittleness.** See Table III.

**Melt Index.** See Table II.

**Mechanical Properties.** See Table III.

**Ultra-Drawn Polyethylene.** See Refs. (70–79).

V / 20 PHYSICAL CONSTANTS OF POLY(ETHYLENE)

*Molecular Properties of Typical Poly(ethylenes).* (63)

Polymer	$\bar{M}_w \times 10^{-3}$	Density (gm/cm <sup>3</sup> )	Groups per 100 Carbon Atoms				
			CH <sub>3</sub> -	-CH <sub>2</sub> CH <sub>3</sub>	-CH=CH <sub>2</sub>	-CH=CH-	=C=CH <sub>2</sub>
Ziegler	50-60	0.960	3.6	0.5	0.09	< 0.02	0.06
Phillips	50-60	0.965	3.1	0.8	1.58	< 0.02	0.08
Solution polymerization	50-60	0.964	3.2	0.5	0.42	< 0.02	0.03
Phillips catalyst gas phase	350	0.954	2.8	< 0.2	0.65	< 0.02	0.04
Low-density PE		0.918-0.928	20-33	6-9	0.08-0.25	< 0.02-0.06	0.17-0.33

*Neutron Scattering Spectra.* See Refs. 83-85.

*Nuclear Magnetic Resonance.* See Ref. 86-97.  
*Solid State.* See Ref. 98.

*Permeability and Diffusion Constants.* See corresponding table in this Handbook and also Refs. 99,100

*Permeabilities at 20°C of High Pressure Poly(ethylene)\* (101)*

Liquids	$g/d (1.6 \text{ cm}^2)^b$	Gases	$\text{cm}^3(\text{NTP}) / (\text{kPa.s})^c$
36% HCl	1.32	Nitrogen	1.6
Methanol	1.86	Oxygen	5.2
Lemon oil	6.2	Hydrogen	9
Acetone	10.5	Carbon dioxide	21
Cyclohexane	389	Ethylene oxide	215
Diethyl ether	485	Water Vapor <sup>d</sup>	0.045 <sup>d</sup>

\* Density(d) = 0.92 g/cm<sup>3</sup>.

<sup>b</sup> For a film 25  $\mu\text{m}$  thick.

<sup>c</sup> For a sample 1 cm( $\times 10^{-10}$ ) thick, to convert kPa to mm Hg, multiply by 7.5.

<sup>d</sup> In g/(kPa.d) for a sample 1 mm thick.

*Refractive Index cont'd*

*Properties of a Series of Selected Poly(ethylene) Samples.*  
See Table II.

*Dependence of Refractive Index on Chain Branching,  
Crystallinity and Density.*  
See Chain Branching

*Properties of Typical Poly(ethylenes).* See Table III.

*Specific Refractivity.*  $r = v \left( \frac{n^2 - 1}{n^2 + 1} \right)$  where  $v$  and  $n$  are specific volume and refractive index, respectively. (6).

Temp. [°C]	$v[\text{cm}^3 \text{ g}^{-1}]$	$n$	$r$
------------	---------------------------------	-----	-----

LOW DENSITY POLY(ETHYLENE) (ALATHON-10)

<i>Refractive Index, <math>n_D^{25}</math></i>			
LDPE,	1.51	111	90      1.159      1.4801      0.3293
MDPE,	1.52	111	100     1.178      1.4693      0.3283
HDPE, (melt index above 0.1)	1.54	111	108     1.209      1.4575      0.3297
Amorphous, $n_{5461}^{25}$	1.49	112	113     1.239      1.4432      0.3286
Crystal; $\alpha \approx \beta$	1.520	112	118     1.250      1.4392      0.3289
$\gamma$	1.582	109	124.4    1.256      1.4368      0.3288
			Avg. 0.3290
HIGH DENSITY POLY(ETHYLENE) (MARLEX 50)			
	130	1.261	1.4327      0.3273
	139.9	1.270	1.4297      0.3297
	150.6	1.281	1.4261      0.3283

( $\alpha$ ,  $\beta$  and  $\gamma$  are refractive indices along the a,b and c crystallographic directions of the crystal).

## V / 22 PHYSICAL CONSTANTS OF POLY(ETHYLENE)

*Thermodynamic Properties (cont'd)*

For linear, branched, amorphous, crystalline and molten poly(ethylene), from 0–600K, see Table "Heat Capacity of High Polymers" in this Handbook and also Refs. 17,46.

For the entropy, enthalpy and Gibbs free energy of various types of poly(ethylene), from 0–600K, see Refs. 17,46.

**Transition and Relaxation Temperatures.** There is considerable disagreement in the literature on the phenomena associated with the various transition and relaxation temperatures observed. Transition temperatures and temperatures associated with peaks in dynamic loss are collected together under the above combined heading. The transition and relaxation tem-

peratures associated with amorphous regions of branched and linear poly(ethylenes) are designated as  $\alpha$ ,  $\beta$ ,  $\gamma$ , etc. in the descending temperature order. (141).

Designation	Temperature Range (°C)	Approximate Activation Energy (kJ mol <sup>-1</sup> )
$\alpha$	60 to 80	> 420
$\beta$	-20 to -30	160–200
$\gamma$	-80 to -90 <sup>a</sup>	46–75
	-120 to -130	32

<sup>a</sup> These frequently merge depending upon the crystallinity and frequency of the test method.

*Frequency Dependence of Relaxation Temperatures in Dynamic Mechanical Loss Measurements. (143).*

$\alpha$	$\beta$		$\gamma$		
Hz	T (K)	Hz	T (K)	Hz	T (K)
HIGH PRESSURE, BRANCHED POLY(ETHYLENES)					
0.3	340	0.3	268	1.25	140
1.2	327	4.1	268	8.6	166
39	333	150	253	324	158
150	355	540	265	$1.2 \times 10^3$	165
200	360	520	280	$1.15 \times 10^3$	165
600	385	6000	320	$1.9 \times 10^4$	$\leq 200$
$4 \times 10^4$	$\geq 360$	$4 \times 10^4$	275	$4 \times 10^4$	180
$1 \times 10^5$	$\geq 320$	$1 \times 10^5$	283	$1 \times 10^5$	$\leq 190$
—	—	$1 \times 10^5$	285	$1 \times 10^5$	200
—	—	$5 \times 10^5$	285	$5 \times 10^5$	205
$2 \times 10^6$	360	$2 \times 10^6$	295	$2 \times 10^6$	210
—	—	$2 \times 10^6$	300	$2 \times 10^6$	210
LOW PRESSURE, LINEAR POLY(ETHYLENES)					
0.3	373	—		1.25	153
0.2	368	8	273	10	173
$\leq 460$	$\geq 380$	$1.1 \times 10^3$	295	840 and $1.57 \times 10^3$	175
3000	420	—		—	—

**Viscosity-Molecular Weight Relationship.** See corresponding table in this Handbook and Ref. 6.

TABLE II: PROPERTIES OF A SERIES OF SELECTED POLY(ETHYLENE) SAMPLES

Sample No.	Optical Melting Point [°C]	Density <sup>1</sup> [g cm <sup>-3</sup> ]	per 100 C Methyl	Infrared Functional Groups per 2000 C			
				Vinyl	Trans-unsaturation	Vinylidene	Carbonyl
PE 1	104.2	0.9142	3.68	0.18	0.15	0.79	0.13
PE 2	112.4	0.9225	2.59	0.32	0.11	0.32	0.02
PE 3	112.2	0.9218	2.48	0.10	0.06	0.29	0.05
PE 4	113.7	0.9232	2.55	0.11	0.06	0.29	n.d.
PE 5	114.0	0.9219	2.46	0.11	0.05	0.30	0.01
PE 6	114.5	0.9228	2.31	0.06	0.05	0.26	n.d.
PE 7	113.5	0.9207	2.59	0.11	0.06	0.33	0.02
PE 8	112.0	0.9188	2.54	0.10	0.06	0.31	n.d.
PE 9	121.5	0.9334	1.40	0.04	0.02	0.11	0.87
PE 10	135.8	0.9549	0.1	1.82	0.04	0.15	<0.005
PE 11	—	0.9554	0.165	0.86	—	0.17	—

## PROPERTIES OF A SERIES OF SELECTED POLY(ETHYLENE) SAMPLES cont'd

Sample No.	Molecular Weight		Intrinsic Viscosity <sup>2</sup> [ml g <sup>-1</sup> ]	Melt Index <sup>3</sup>	Melt Viscosity <sup>4</sup> [Pa s]	Elastic Compliance <sup>5</sup> [MPa <sup>-1</sup> ]
	Weight Ave.	Number Ave.				
PE 1	510,000 <sup>6</sup>	10,700 <sup>10</sup>	79.5	1.80	64	$63 \times 10^{-6}$
PE 2	300,000 <sup>6</sup>	13,300 <sup>10</sup>	75.7	1.95	38	46
PE 3	550,000 <sup>6</sup>	19,100 <sup>10</sup>	96.1	0.16	620	46
PE 4	225,000 <sup>7</sup>	(16,000) <sup>9</sup>	62	19.9	24	22
PE 5	500,000 <sup>7</sup>	(18,000) <sup>9</sup>	75	3.30	185	36
PE 6	500,000 <sup>7</sup>	(22,000) <sup>9</sup>	82	1.06	73	54
PE 7	300,000 <sup>7</sup>	(45,000) <sup>9</sup>	77	2.94	23	31
PE 8	800,000 <sup>7</sup>	(55,000) <sup>9</sup>	97	0.21	310	54
PE 9	300,000 <sup>7</sup>	(27,000) <sup>9</sup>	73	3.75	153	$39 \times 10^{-6}$
PE 10	144,000 <sup>6</sup>	11,500 <sup>10</sup>	116	2.92	—	—
PE 11	—	—	—	—	—	—

Notes: 1. Samples annealed 1 hour at about 100°C.

2.  $\alpha$ -Chloronaphthalene, 125°C.

3. ASTM D-1238-57T.

4. Newtonian melt viscosity at 150°C and 400 Pa.

5. Steady-state elastic compliance from creep recovery at 150°C and 400 Pa.

6. Light scattering after optical clarification by high temperature ultracentrifugation.

7. Preliminary value, subject to revision.

8. Measured by osmometry.

9. "Best guess." Subject to drastic revision.

10. Cryoccopy.

TABLE III: PROPERTIES OF TYPICAL POLY(ETHYLENES) (6,144,145)

Property	Low Density ASTM Type I <sup>a</sup>	Medium Density ASTM Type II <sup>a</sup>	High Density ASTM Type III <sup>a</sup>
Abrasion resistance, Taber, [mg/1000 cycles]	10-15	6-10	2-5
Brittleness, low temperature, [°C]	< -118	< -118	< -118 to -73
Coefficient of thermal expansion $\times 10^{-5}$ (D696) [K <sup>-1</sup> ]	10	—	13
Density (D792) <sup>b</sup> , [g cm <sup>-3</sup> ]	0.910-0.925	0.926-0.940	0.941-0.965
Dielectric constant at 1 kHz (D150)	2.28	—	2.32
Elongation at break (D638), [%]	150-600	100-150	12-700
Hardness, Shore D (D1706)	44-48	45-60	55-70
Impact strength, Izod (D256), [ft lb/in notch]	> 16	> 16	0.8-14
Power factor at 1 kHz (D150)	< 0.0001	—	< 0.0001
Heat capacity, [kJ kg <sup>-1</sup> K <sup>-1</sup> ]	1.916	1.916	1.916
Tensile modulus (D638), [MPa] = [N mm <sup>-2</sup> ]	55.1-172	172-379	413-1034
Tensile strength (D638), [MPa] = [N mm <sup>-2</sup> ]	15.2-78.6	12.4-19.3	17.9-33.1
Heat softening temp. (D1525), [°C]	88-100	99-124	112-132
Volume resistivity (D257), [cm]	$6 \times 10^{15}$	—	$6 \times 10^5$

<sup>a</sup>ASTM designation D1248-72, "Standard Specification for Polyethylene Plastics

olding and Extrusion Materials."

<sup>b</sup>Numbers in parentheses refer to the ASTM Standards, American Society for Testing Materials.